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EMPLOYMENT OF TOXIC SUBSTANCES AS A MILITARY ARM. REQUIREMENTS. STUDY OF THE β,β-DICHLOROETHYL SULFIDE

A THESIS

Presented to

the Faculty of the Graduate Division

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In Partial Fulfillment

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Master of Science in Chemical Engineering

By

Ernesto Eduardo Bonta'

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EMPLOYMENT OF TOXIC SUBSTANCES AS A MILITARY ARM.
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May. 1, 1958.

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CHAPTER I

INTRODUCTION

The use of war gas in 1915 opened a new field of study in the chemistry of war, that of war gases. The chemistry of war for many years was confined to the study of explosives, and it underwent a new development when substances which had an offensive action on human and animal organisms were used in war.

This started the study of war gas, which has become one of the most complex and important departments of chemistry and chemical engineering.

As nearly all chemical compounds exert some toxic effects, either local or general, upon the body, it is impossible to estimate with accuracy the total number of toxic substances. However the limited number of substances which are usefully employed during the war or standardized after testing, in comparison with the huge number of substances studied for such purposes, gives an indication of the difficulty of this selection.

This study tries to establish a systematic approach to the study of a substance to be used as a war gas in an attempt to simplify the complicated and long-lasted problem of selection. Mustard gas or β,β-dichloroethyl sulfide is thoroughly studied through a systematic approach that involves several steps:

(1) Theoretical study of the chemical structure of the substances and their relationship to the physiological properties.

(2) Determination of the ideal properties of a war gas and comparison of the properties of the substance under study with the ideal ones.

(3) Laboratory and field testing.

CHAPTER II

REQUIREMENTS FOR A SUBSTANCE USED AS A CHEMICAL AGENT

The principal characteristics to be considered in evaluating the practical utility of a substance for use as a war gas are as follows:

A. Physical Properties

Vapor Density.--Vapor density is the ratio of the density of a given gas, generally air, under standard conditions of temperature and pressure. It is of some value in providing information as to the probable persistency of a war gas; it is known that the rate of diffusion of a gas is inversely proportional to the square root of the density. For this reason a war gas of low vapor density will tend to disperse sooner than one of higher vapor density. However, air currents and other influences tend to offset any effects of diffusion or vapor density, especially when the war gas has been diluted by air.

Liquid and Solid Densities.--These densities are of interest only in computing the chemical efficiency of a munition, that is, the ratio of the weight of the filling to the total weight of the filled munition. The higher the density, the higher the chemical efficiency of a munition.

Melting and Freezing Point.--These affect the design, functioning and ballistics of the munition and also in the case of solid or liquid agents it is important to know the freezing and melting point because:

(1) In order to secure uniformity in ballistic effects and dispersion of the munition, it is necessary to keep the chemical filler in one physical state.

(2) The vapor pressure of the solid below the freezing point is usually too low to permit using the agent for vapor effect.

These considerations are of considerable importance if these points occur within the range of ordinary atmospheric temperatures.

Boiling Point.--An estimation of the persistency of a war gas may be made when its boiling point is known. The higher the boiling point the lower the vapor pressure and the greater the persistency at ordinary temperatures and the less the pressure generated in the container in storage. Due to the last fact, a smaller void may be employed in filling the shell and loss leakage is apt to occur in storage and handling. It must be considered also that the higher the boiling point, the greater the explosive charge required effectively to disperse the substance, using munition to disseminate, and the less chemical will be contained in the shell.

Vapor Pressure.--Evaporation is constantly taking place from the exposed surfaces of all liquids and solids. Because of this tendency a layer of vapor forms above each substance and exercises a certain pressure whose magnitude depends on the temperature. This pressure is termed "vapor tension." When the vapor is in equilibrium with the solid or liquid it is said to be saturated and the equilibrium pressure is called "the vapor pressure." It is one of the most important properties in fixing the tactical usefulness and persistency of a war gas. This property

has only a minor value in the case of substances which are used in the form of aerosols.

Volatility.--This is the weight of vapor present in a unit volume of air, under equilibrium conditions, at a specified temperature. The volatility varies with temperature, and Herbst (1) has established the following approximate relationship between temperature and volatility. "Between 10°C and 30°C an increase in temperature of one degree causes an increase in volatility of about ten per cent."

The volatility (v) of a substance at a given temperature may be easily calculated from the following formula (1):

$$v = \frac{273 \times 10^6 \times m \times p}{22.4 \times (273 + t) \times 760}$$

where

p = vapor pressure at temperature t (mm. of mercury),

m = molecular weight (grams)

t = temperature (°C).

Volatility is also an important property since it determines the maximum concentration which can exist in the open air at any given temperature.

Latent Heat of Vaporization.--This is the heat required to change one gram of liquid into vapor without change of temperature. This property is very important because it is the main factor in determining the behavior of certain substances at the moment of release from shells or bombs. When the munition bursts the contents may be rapidly transformed into vapor and the heat is absorbed from the surroundings. This results in the cooling of the war gas, causing the vapor to settle. Since the

heat of vaporization of the different war gases varies somewhat, some show the desirable settling effect to a greater degree than others. The greater the latent heat of vaporization the higher the settling effect.

Persistency.--This is the time during which a substance can continue to exercise its action in an open space, that is, during which it is capable of producing casualties among unprotected personnel. The physical reasons for the great differences in the persistence of war gases are due to the fact that these substances have very different vapor pressures and to the degree to which these pressures vary on change of temperature. The higher the vapor pressure of a substance is at a given temperature of the air, the less persistent it is at that temperature. The following formula has been proposed for calculating the persistency of a war gas (2).

$$s = \frac{c_1}{c} = \frac{p_1}{p} \frac{m_1 t}{m t_1}$$

where

s = persistency of the substance,

c = velocity of evaporation of the substance at absolute temperature t,

c_1 = idem of water at 15°C,

p = vapor pressure of the substance at t,

p_1 = idem of water at 15°C,

m = molecular weight of the substance,

m_1 = idem of water,

t = absolute temperature of the air,

t_1 = absolute temperature corresponding to 15°C.

Actually this formula gives accurate values for the time which a substance takes to evaporate compared with the time taken by the same quantity of water at 15°C in the same conditions.

The war gases are classified according to persistency as follows (3):

(1) Persistent.--Persistent war gases are those which are effective in either the liquid or solid form at point of release for more than ten minutes under field conditions.

(2) Non-persistent.--Non-persistent war gases are those which are effective in vapor or aerosol form at point of release for a period of less than ten minutes under field conditions. The non-persistent gases exist only as vapor after being released from munition.

B. Chemical Properties

Chemical Stability.--Stability in storage determines the practical usefulness of a chemical agent since, if it decomposes in storage, it will have little value regardless of any other properties which may recommend it.

Hydrolysis.--This is the reaction of any chemical substance with water whereby one or more new substances are produced.

Rate of Hydrolysis.--This determines the resistance of the various war gases to decomposition by water. If a compound rapidly hydrolyzes it not only greatly reduces its effectiveness in the field but seriously complicates its storage and loading into munitions. Hence, rapid hydrolysis is an important factor in lowering the persistency of war gases.

Hydrolysis Products.--In certain cases, hydrolysis does not destroy the toxicity of a war gas because the product of the hydrolysis is also toxic. With the exception of toxic products, hydrolysis products are of little importance in the study of war gases.

Action on Metals, Plastics or Fabrics.--The action of a chemical agent or war gas on certain materials acts as a limitation to use of the agent. For example if a war gas acts corrosively on commonly used container metals, it will be difficult and prohibitively expensive to use it. This corrosive action requires the employment of special expedients such as protection of the metal walls of the container with a layer of some protective substance or employment of a supplementary container which isolates the war gas from the walls of the container.

C. Physiological Effects

The one indispensable requisite of a substance for use as a war gas is that it should have powerful physiopathological qualities. It may have various types of action, lachrymatory, suffocating, vesicatory, etc.

In order to express an opinion on the practical utility of a substance as a war gas on the basis of its physiopathological properties, it is not sufficient merely to know that the substance has a toxic effect on the organism but also to know the degree of its action. It is therefore necessary to determine the quantity of the substance which must be present in the air to obtain the desired action on the human or animal organism exposed during a certain time.

These two factors, concentration of the toxic substance and time of exposure to the toxic substance determine the effectiveness of a gas (toxicity). Due to this fact, the degree of toxicity of a war gas is expressed in terms of dosage (c x t).

Dosage.--This is the concentration of war gas to which a man or animal is subjected multiplied by the length of exposure (3).

$$\text{Dosage} = c \times t$$

where

c = concentration of a war gas (mg/m^3),

t = time of exposure (minutes).

Thus the c x t product expresses in a single figure the interrelationship of concentration and the duration of the exposure of war gases which exert their effects in vapor or aerosol form. Since dosage is a combination of two factors, for most war gases the same effect can be attained by exposure to a high concentration for a short time or to a lower concentration for a longer time. This product varies inversely as the toxicity of the substance, i.e., the smaller the value of dosage, the more toxic is the substance (considering the same effect).

As to the effect produced on men or animal body, the following definitions complete the study of war gases from the point of view of toxicity.

Median Lethal Dosage.--This is the dosage which will kill fifty per cent of an exposed group of subjects (usually the term refers to unprotected man).

Median Incapacitating Dosage.--This is the dosage required to render fifty per cent of unprotected individuals exposed incapable of effectively performing their duties.

Actually an individual may receive an amount of war gas that is less or more than expected for a given dosage, depending upon some of the following variables:

(1) How long the breath was held during short exposures,

(2) Whether the war gas was also absorbed through the skin,

(3) Whether the war gas stimulated rate of breathing,

(4) Amount of physical exertion of the individual at time of exposure,

(5) Rate and depth of breathing of individual at time of exposure,

(6) Rate of detoxification, especially if exposure was long.

For purpose of tabulation, such variables are ignored and the dosage values are assumed to measure the amount of war gas received by an individual breathing at a normal rate in a temperate climate with average humidity. These values provide a basis of comparison for the war gases. The rate of detoxification (rate at which the body is able to change a poisonous substance into a harmless one or to eliminate it directly) is an important factor in determining the hazards of repeated exposure to low concentrations of toxic gases. Some war gases are not detoxified at any detectable rate by the human body. Such war gases are cumulative in their effects. For example, an exposure of one hour to one of these gases, followed within a few hours by another exposure of one hour has approximately the same effect as a single exposure of

two hours' duration. The disabling or lethal dosage in the case of such war gases is proportional to the time factor within reasonable limits. Other substances are detoxified by the human body at a measurable rate.

Absorption of the War Gas.--Next to toxicity the manner in which a gas exerts its action upon the body is the most important consideration. Many gases have more than one mode of action. In general the more extensive the mode of action and the way of absorption of a gas, the more valuable it is from a military viewpoint.

Rate of Action.--There is a wide variation in the rate of action to the toxic war gases, even to those of similar classifications. Some substances act with remarkable speed in producing effects upon the body, while others act very slowly, and their effects are not noticeable until many hours after exposure.

From a very general viewpoint and regardless of the type of gas, it is obvious that the quicker it produces its effects, the sooner it secures the desired results.

D. Military Properties

Before going on in the study, it is necessary to define the manner and conditions in which the war gases are employed in the field and the desired effects (production of casualties). There are two main tactical situations in the field: the offense and the defense. Since, according to the tactical situation the requirements which a war gas must meet are different, we may summarize this subject by stating the qualities and characteristics of an ideal gas of each type (offensive and defensive).

Offensive gas

Physical properties

(1) Volatility (maximum field concentration)

(2) Invisibility

(3) Lack of odor

(4) Boiling point as low as possible

(5) High vapor pressure

(6) High solid or liquid density

(7) Melting point above maximum atmospheric temperature (solid) or freezing point below minimum atmospheric temperature (liquid).

(8) Low persistency

Chemical properties

(1) Chemical stability

(2) Non-hydrolyzable

(3) Withstands explosion without decomposition

Physiological effects

(1) High toxicity

(2) Multiple effectiveness

(3) Effects of maximum duration

(4) Immediate effectiveness

(5) Insidiousness in action

(6) Null or very low rate of detoxification

Other properties

(1) Penetrability

(2) Ease of manufacture

(3) Availability of raw materials

(4) It must be capable of being disseminated from a device practicable for field use in sufficient concentration to produce the effect desired.

(5) It should be difficult to protect from it and to detect by ordinary methods available.

(6) The mechanism of action, protective measures and method of treatment for the agent should be known.

Defensive gas

The ideal war gas for use on the defensive should also meet the above requirements except that it should be persistent rather than non-persistent and it should be effective in low concentrations.

CHAPTER III

RELATION BETWEEN CHEMICAL STRUCTURE AND AGGRESSIVE ACTION

A. Influence of Different Atomic Groups and Molecular Structure

The chemical composition of a chemical warfare agent is not necessarily of interest to the military but to the research worker it furnishes further opportunity for the study of the relationship between chemical constitution and physiological properties. Certain generalizations have been drawn which show that certain chemical groupings occur frequently among chemical warfare agents.

However, just as the long unsuccessful search by pharmacologists for a relationship between structure and physiological activity that could be used for predicting new types of drugs, so there has been no success in predicting chemical warfare use of a compound from its structure.

Once a compound has been discovered that has suitable toxic properties, it is true that search of related compounds may yield certain homologues or analogues that have properties desirable for certain uses. This is illustrated by the following examples: series of tri-valent arsenic (methyl dichloro arsine, diphenylchloro arsine, lewisite or (2-chlorovinyl) dichloro arsine); series of mustard gas and series of trilons.

Intensive work of molecular groupings have been made, but owing to the short period which this has been prosecuted, as well

as the secrecy which has surrounded the results, it is not yet possible to state general laws with any certainty.

However, it will be of interest to give an account of the observations and hypotheses published on the influence of the structure of these substances and in particular of the introduction of certain atoms or radicals on the nature of the action exerted.

The majority of the substances employed or standardized as war gases are organic.

Among the inorganic compounds employed were chlorine, bromine, arsenic trichloride, etc. These, though having relatively little aggressive power, were used at the beginning of gas warfare because of the ease of their manufacture and the simplicity of their application. Various other inorganic products, such as arsine, stibine or phosphine although very toxic, have not been used or standardized as war gases due to their unsuitable physical properties.

The organic substances having toxic action usually contain atoms of halogen, sulfur or arsenic or radicals such as $-NO_2$ or -CN in their molecules. It is to the presence of these atoms or radicals as well as to the molecular structure that physiological action is nowadays attributed.

Influence of Halogen Atoms.--The halogens themselves have noxious action on the animal organism and this diminishes in intensity in passing from fluorine to iodide; the tendency to combine with hydrogen also diminishes with increase in atomic weight. The introduction of halogen into the molecule confers aggressive properties which vary according to the nature of the halogen and the number of halogen atoms introduced.

With regard to the influence of the nature of the halogen, it has been observed that the lachrymatory power of halogenated substances increases with increase of the atomic weight of the halogen present. However, as it has been pointed out above, the truly toxic action varies inversely as the atomic weight of the halogen.

In considering the influence of the number of halogen atoms present it is found that while one halogen atom confers predominantly lachrymatory properties on the molecule, an increase in the number of the halogen atoms diminishes the lachrymatory but increases the asphyxiant action. A typical example of this observation is the series of halogenated esters of formic acid. This law does not always hold true, however, with some substances as mustard gas it is found that the introduction of further halogens first diminishes and then destroys the aggressive properties of the original compound.

The position occupied by the halogens in the molecule also has a notable influence on the aggressive properties of the original compound. In the aliphatic series it is found that compounds with the halogen in the β position are more powerful lachrimatories than their isomers which have the halogen in the α position. In the aromatic series it is observed that the introduction of a halogen atom into the side chain of a substance confers lachrimatory properties, while if it replaces a hydrogen atom from the benzene nucleus, a substance results which has no physiological properties.

This difference in physiopathological properties is probably connected with a difference in the mobility of the halogen atom.

The halogen must not be bound in too labile a manner to the molecule; otherwise it will be attacked by atmospheric agents or by the surface of the organism before the entire molecule has penetrated the cells. Neither may it be bound to the molecule in too stable a manner; otherwise the substance will be practically inert, for the atom will not even be detached in the interior of the organism.

Influence of the Sulfur Atom.--Sulfur is not generally considered as a toxic element in the same way as are the halogens. Nevertheless, its presence seems to confer on a substance the capability of penetrating the epidermis, which explains the actual aggressive properties of such compounds.

An example of this observation is found in a comparison of substances containing a sulfur atom with their analogues which contain oxygen (mustard gas and analogue which contains oxygen).

Comparatively few war gases contain sulfur in their molecules. It is generally observed that the degree of toxicity of the sulfur compounds varies with the valency of the sulfur atom and with the nature of the radicals with which the sulfur is united. Among the sulfur compounds those of the type R_2S (divalent sulfur) are more toxic than those of the type R_2SO (tetravalent sulfur) and far more than those of the type R_2SO_2 (hexavalent sulfur).

Those compounds in which the sulfur has a specific function also contain halogen atoms.

Little is known regarding the influence on the aggressive properties of a substance of the introduction of a sulfur atom.

Influence of the Arsenic Atom.--The arsenic atom also imparts toxic properties to a higher degree than the sulfur atom. It is a general rule that substances containing a trivalent arsenic atom have a considerably greater physiological action than those containing a pentavalent arsenic atom.

The arsenical war gases contain halogen atoms or organic radicals such as -CN, -SCN, etc., besides the arsenic atom.

The nature of the aggressive action depends on the number and the nature of the organic radicals with which the arsenic atom is linked.

In general, arsenical compounds have an aggressive action when two of the three valences of the arsenic atom are linked to like atoms or groups and the third to a different atom or radical. If the three valences of the arsenic atom are linked to similar atoms or radicals the compound has practically no aggressive action.

In particular it may be observed that arsenic substances with a single organic unsaturated radical have a more powerful vesicatory action than those with two or more organic radicals. It may also be noted that when the arsenic atom is linked to an alkyl or phenyl group, substances with predominantly irritant action are obtained. This action is accentuated in compounds containing two such radicals linked to the arsenic atom.

Influence of the Oxime Group.--The oxime group is generally considered as having no toxic properties, but of being capable of confering orticant properties on substances containing it.

Influence of the -CN Group.--To the -CN group two different structures are attributed: one; -C ≡ N, the nitrile; the other -N = C =, the isonitrile grouping.

It has been observed that compounds containing the isonitrile group have more powerful toxic properties than those containing the nitrile. This difference in biological properties can be compared with the greater facility with which compounds containing the isonitrile radical liberate hydrocyanic acid.

The presence of a second CN group generally diminishes the aggressive properties of a substance and the presence in the same molecule of this group and of other atoms such as halogens while reducing the toxic action confers highly lachrimatory properties.

Influence of the Nitro Group.--The aggressive properties conferred on a substance by the introduction of the nitro group depend on whether the group combines through an oxygen or a carbon atom, that is, whether a nitrate or a nitro compound is produced. The nitrates have not been used or standardized as war gases, but very efficient agents are included among the nitro derivatives.

In particular the introduction of the NO_2 group confers lachrimatory properties or increases any such tendency if it is originally present in the molecule.

Influence of Molecular Structure.--According to various observations, the aggressive action of a substance depends not only on the presence of particular atoms or radicals in the molecule, but also on the molecular structure and in particular on:

(1) The presence of unsaturated bonds. This presence usually involves an increase in the toxic properties (This observation was first made by Loew (1) in 1893). For example, acrolein (CH_2 = CH-CHO) has strongly irritant properties, while the corresponding saturated aldehyde is innocuos.

(2) The molecular symmetry. It has been observed that substances with symmetrical molecules generally have a more powerful aggressive action than asymmetrical substances. For example symmetrical dichloroacetone

$$\begin{array}{l} CH_2Cl \\ CO \\ CH_2Cl \end{array}$$

has great irritant power while the asymmetrical compound is almost completely lacking in irritant properties.

$$\begin{array}{l} CH_3 \\ CO \\ CHCl_2 \end{array}$$

B. Theories of General Nature

General theories regarding the relation between chemical structure and physiopathological action have been elaborated with especial reference to the war gases. From among the many published, the Meyer's theory and the Toxophor-Auxotox theory are the best known (4).

Meyer's Theory.--According to this theory the physiopathological action of war gas is attributed to certain atoms or radicals which have a

tendency to react easily with other substances by addition. This classification on the basis of their ease of reaction should be determined by their combination with the various biological entities or tissues (as the blood, the nerve cells, the respiratory epithelia, etc.) which undergo specific and characteristic alterations.

In other cases, Meyer suggests, the aggressive action may be attributed to the capacity of the entire molecule of forming additive compounds with vital constituent of the organism.

Toxophor-Auxotox Theory.--The theory of toxophors and auxotoxes, first elaborated by Ehrlich (5) for toxic substances and later applied by Nekrassov (6) to the war gases, attributes the physiopathological properties of these substances to special atoms or radical in a similar manner to Witt's theory regarding the color of organic substances.

The war gases, according to Nekrassov, have structures analogous to those of colored substances. By examining the chemical structures of the war gases, certain atomic groups are found which confer on substances the potentiality of becoming war gases, in the same way Witt found certain groupings common to colored substances. The groupings found in war gases are called "toxophors" (chromophores).

Such are, for example: CO; S ; C C ; N $\overset{O}{O}$; N C; As ; etc.

There also exist other groups capable of communicating the characteristic toxic functions of the toxophoric, that is of transforming into actuality the latent capacity of the toxophor group. These groups are named auxotoxes (auxochromes) and may be either atoms

(halogens, oxygen, etc.) or atomic groups ($-NH_2$, benzil, phenyl, methyl, ethyl radicals, etc).

According to this theory, just as in colored substances the introduction of some auxochromic groups changes the color of the substances, so in the war gases the presence of certain auxotoxes can alter the type of biological action (for example introduction of halogen into the hydrocyanic molecule).

Also the auxotoxic group in the war gases, like the auxochromes in colored substances differ in their action according to their position in the molecules (for example halogens differ in their influence according to whether they are in a methyl or an ethyl group).

However, this theory cannot be applied so generally to the war gases as Witt's to colored substances. In war gases the auxo group may function either positively or negatively; increase in molecular complexity does not lead to increase in the toxicity, etc.

Furthermore this theory, like that of Meyer already described, though having many interesting aspects, does not sufficiently explain the behavior of some of the war gases.

CHAPTER IV

TYPICAL STUDY--β,β-DICHLOROETHYL SULFIDE

A. General

The main object of this section is to study β,β-dichloroethyl sulfide (mustard gas) making a comparison of its properties with the ideal properties of a war gas established in the first part of this work and through this study, determine the feasibility of mustard gas for use as a war gas.

This section develops a methodical and theoretical study to qualify a substance as a war gas.

After this step it is necessary to test the substance in the laboratory and field to check its behavior.

The term "mustard gas" is an unfortunate one, due to the fact that the chemical agent or war gas is often confused with the true natural mustard oil which is prepared from black mustard seed and is chemically allyl isothiocyanate.

It is probable that mustard gas was first made in 1822 by Despretz (1) in his study of the reaction between sulfur chloride and ethylene,but his product was not clearly characterized. In 1860 it was independently prepared by Guthrie and Niemann (2) by passing ethylene into sulfur chloride. In 1866 the German chemist Victor Meyer (2) prepared mustard gas by the action of hydrochloric acid and thiodiglicol, and described the effect of the product. Finally in 1891 the opthalmologist Theodore Leber made a study of the toxicity of mustard gas (7).

Increased knowledge concerning the properties of mustard gas and of its manufacture took place during the first world war and it was employed by both Germans (first) and the Allies (later) with great success.

B. Physical Properties

Pure β,β-dichloroethyl sulfide is a colorless, neutral-to-litmus, oily liquid. In the crude state, it is brown and has a characteristic odor (garlic-like).

Molecular Weight.--159.08

Vapor Density.--(compared to air) 5.4

Liquid Density.--1.27 at 68°F (20°C)

Solid Density.--1.37 at 32°F (0°C)

The variation in density per degree between 15°C and 90°C is 0.001058. The variation in volume of one gram per degree between the same temperature is 0.0006895 cc. The variation in volume in cubic centimeter per degree is 0.000881 (3).

Freezing Point.--58°F (14-15°C). It is desirable to add to mustard gas a small percentage of solvent to keep it in a liquid state for all temperatures ordinarily encountered in the field.

Solubility.--Mustard gas is very sparingly soluble in water, its solubility increasing to a certain limit with increase in temperature. According to Hopkins (8), the solubility in water is 0.033 per cent at 0.6°C and 0.07 per cent at 10°C. According to French data (2) the solubility at 25°C is 0.047 per cent; American data (3) gives 0.069 per cent.

It is very soluble in various hydrocarbons and organic solvents such as kerosene (in which it is soluble in all proportions at 26°C), petrol, carbon tetrachloride, monochlorobenzene, ethyl alcohol, ethyl ether, carbon disulfide, thiodiglicol, glycerol (9).

It is also soluble in animal and vegetable oils and fats and only slightly in vaseline and paraffin wax.

To lower its freezing point the following solvents may be used: some easily volatile solvents (carbon tetrachloride, chlorobenzene, or nitrobenzene) or chloropicrin, with the additional advantage that the solvent is toxic.

Boiling Point.--Some authors give 217°C; others 222.5°C (atmospheric pressure). Its boiling point has been reported as 97°C at 10 mm.; 98°C at 10 mm.; 104-105°C at 13 mm.; 105°C at 14 mm.; 107°C at 15 mm.; 120°C at 34 mm. and 122.5°C at 37 mm. (9).

Vapor Pressure.--0.072 mm. of mercury at 68°F (20°C)

The vapor pressure of mustard gas at various temperatures may be calculated from the following formula (1).

$$\log p = 8.397 - \frac{2734.5}{t}$$

where

p = vapor pressure of mustard gas at t,

t = absolute temperature.

Volatility.--22 mg/m^3 at 0°F; 47 mg/m^3 at 32°F (0°C); 95.8 mg/m^3 at 68°F (20°C); 3,660 mg/m^3 at 104°F (40°C) (3).

Flash Point.--221°F

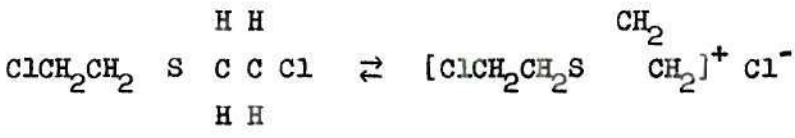
Latent Heat of Vaporization.--94 calories per gram

Persistency.--High persistency

C. Chemical Properties

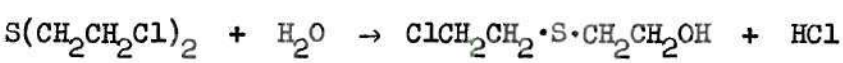
Mustard gas can be the starting material for many syntheses, and although the literature on the compound is rather extensive, it would no doubt be larger if it were not for the high toxicity of the substance.

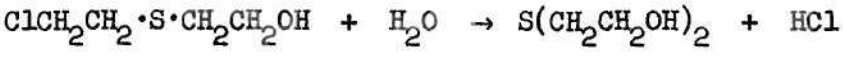
The reactivity of mustard gas is conveniently presented from the standpoint of its electronic structure as



There is considerable evidence that mustard gas is ionized slightly as shown above. The hydrolysis to form thiodiglycol can be completely suppressed by a 17 per cent solution of hydrochloric acid.

Hydrolysis.--It was generally assumed and later proved that the hydrolysis of mustard gas occurs in two stages.





Wilson, Fuller and Schur (9), showed that the hydrolysis is a two-stage reaction which affects only the molecules dissolved in the aqueous phase. The rate of the first stage of the reaction determines that of the second. Once steady conditions are established, the concentration of the intermediate compound automatically increases or

decreases keeping the rate of the second stage just equal to that of the first. The amount of intermediate compound present at any time is extremely small and the time required to build up the equilibrium concentration is generally negligible. The second stage of the hydrolysis reaction is substantially non-reversible except in very strong hydrochloric acid solutions. The first stage is, however, reversible to a considerable extent in the presence of even dilute acids. This reversibility of one stage serves to retard but not to stop the reaction, because the intermediate hydrolysis compound is being continually destroyed by the irreversible second stage.

The velocity of hydrolysis is influenced by various factors such as the time of contact, the temperature, the water-mustard gas ratio, the quantities of acid, alkali and hydrolysis products present, as well as the degree of dispersion of the dichloroethyl sulfide in the water.

It was found that when one part of the sulfide was dissolved in two hundreds parts of water, the ratio of the length of time for complete hydrolysis at 20°C; 50°C and 100°C is 1:7:5:30. A longer time is required if less water is used (9).

In the following table (Table 1), due to Hopkins (8), the degree of hydrolysis is given as a function of the time of contact of the mustard gas with water (20°C is the temperature at which the degree is given).

Table 1. Degree of Hydrolysis

Time (minutes)	Per cent hydrolyzed compared with that dissolved
10	50
20	70
30	79
40	84
50	85
60	85

Acids and ammonium hydroxide (one mole per liter) slightly retard the decomposition and Wilson, Fuller and Shur (9) determined the acceleration of the hydrolysis by alkaline colloidal solutions. These have the effect of increasing the degree of dispersion of the substance.

Stability.--At ordinary temperature mustard gas is a stable compound but on heating at ordinary pressure it decomposes without distilling. This decomposition commences at about 150°C and is complete at 500°C.

$$2S(CH_2CH_2Cl)_2 \rightarrow S_2(CH_2CH_2)_2 + 2C_2H_4Cl_2$$

This reaction is reversible, so that on heating the reaction products to 180°C dichloroethyl sulfide is formed.

Action with Metals.--Aluminum, lead, brass, iron, bronze, zinc and tin are not acted on by mustard gas at ordinary temperatures; with the first three metals no appreciable action is noted at 100°C, but the others named are attacked at this temperature; the action being most rapid in

the case of tin. Then the action on metals or other materials is very little when pure.

D. Physiological Properties

Mustard gas has a triple effect, being a vesicant, lung injurant and lachrimator combined. It acts as a cell irritant and finally as a cell poison.

The first symptoms of mustard gas poisoning usually appear in from four to six hours. The higher the concentration the shorter the interval of time between the exposure to the gas and the first symptoms. The physiological action of this compound may be classified as local and general. The local action results in conjunctivitis or inflammation of the eyes, erytheme (redness of the skin) which may be followed by blistering or ulceration and inflammatory reaction of the nose, throat, trachea, bronchi and lung tissue.

The susceptibility to the toxic action of mustard gas varies with race and also with individuals.

Injuries produced by mustard gas heal much more slowly and are more liable to infection than similar burns produced by other means. This is due to the action of mustard gas in making the blood vessels incapable of carrying out their functions of repair and by the fact that dead or dying tissue acts as a good medium for bacterial growth.

Median Concentration Detectable by Odor.--1.2 mg/m^3

Median Lethal Dosage.--Inhalation: 1500 mg. min/m^3. Skin absorption (masked personnel): 10,000 mg. min/m^3.

Median Incapacitating Dosage.--Eye injury: 200 mg. min/m^3. Skin absorption (masked personnel): 2000 mg. min/m^3 at 70-80°C.

Wet skin absorbs more mustard gas than dry skin does. Above 80°F perspiration causes increased skin absorption. The incapacitating dosage drops rapidly as perspiration increases, at 90°F 1000 mg. min/m^3 could be incapacitating.

Rate of Detoxification.--Not detoxified. Even small repeated exposures are cumulative in their effects. Exposure to spilled mustard gas (factory or filling plants) causes minor symptoms such as red eye. Repeated exposures to such vapors produce one hundred per cent disability by irritating the lungs and causing chronic cough and pain in the chest.

Eyes are very susceptible to low concentrations; higher ones are required to produce incapacitating effects by skin absorption than by eye injury.

Rate of Action.--Delayed. Usually four to six hours until first symptoms appear. Latent periods have been observed, however, up to twenty-four hours and even, in rare cases, up to twelve days.

CHAPTER V

MANUFACTURE OF MUSTARD GAS

A. Processes

Mustard gas may be prepared industrially by several processes, all of which are based on one of the two methods described: Meyer's and Niemann-Guthrie's (10). The most successful procedureusing the Meyer's method is the German process which may be schematically described as follows. Gaseous hydrogen chloride is run into a mixture of concentrated hydrochloric acid and thiodiglicol at a controlled temperature, the mustard gas separates as a lower layer and is run off. The process can be either batch or continuous.

During World War I, the Germans made thiodiglicol from ethylene by converting it to chlorohydrin and treating the latter with sodium sulfide.

$$C_2H_5OH \rightarrow H_2O + CH_2{=}CH_2$$

$$Ca(ClO)_2 + H_2O + CO_2 \rightarrow CaCO_3 + 2HClO$$

$$CH_2{=}CH_2 + HClO \rightarrow ClCH_2{\cdot}CH_2OH$$

$$2OHCH_2CH_2Cl + SNa_2 \rightarrow S\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 2NaCl$$

$$S\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 2HCl \rightarrow S(CH_2CH_2Cl)_2 + 2H_2O.$$

The German process has two outstanding advantages:

(1) The intermediate products have no dangerous properties and hence there is no danger to personnel working in the plants on any of the intermediate steps, and

(2) The yield is relatively high and the product pure.

On the other hand the German process has the objection of being very complicated and only a chemical technique excellently organized and backed by a wealth of experience can successfully resolve the technical difficulties that appear in this method.

Compared with the Meyer process the Niemann-Guthrie method allows the product to be prepared more rapidly and in better yield with less technical problems, but it requires careful control during the course of the reaction.

Several systems of manufacture have been proposed for the preparation of mustard gas by the Niemann-Guthrie method. The most convenient procedure is that of Levinstein, known as the Levinstein process (7).

This is a batch process run in an iron reactor, fitted with an agitator, of six tons capacity. The initial charge is about one ton of product left from the preceding batch; this acts as solvent and a reaction medium for the ethylene and sulfur monochloride that are run in at a slow rate, so arranging the speed of their introduction and the cooling that the temperature of the reaction mixture remains at 30-35°C. A five-ton batch is completed in about eight hours.

By distillation Levinstein mustard gas is found to contain 70 per cent pure mustard gas.

The stoichiometry of the Levinstein process may be schematically represented as follows.

$$2CH_2{=}CH_2 \;+\; S_2Cl_2 \;\rightarrow\; (ClCH_2CH_2)_2S \;+\; \underline{S}$$

The raw materials for the manufacture of mustard gas, using this method, are generally cheap and plentiful. In the United States of America the cost of manufacture was placed at $0.13 per pound in 1945. The introduction of a distillation step, to remove the impurities, raised the cost to about $0.35 per pound.

Mustard gas can also be made on a large scale (French process) by the reaction between ethylene and sulfur dichloride. The reaction is run in a solvent (chlorobenzene or carbon tetrachloride) and the solvent subsequently stripped by distillation.

Sulfur dichloride, however, is such an active chlorinating agent that the resulting product is rather unstable in storage due to the presence of chlorinated mustard. Such compounds split off hydrogen chloride quite easily.

B. Composition of Levinstein Mustard Gas

In the Levinstein process the reaction between ethylene and sulfur monochloride is conventionally represented as follows:

$$2CH_2{=}CH_2 \;+\; S_2Cl_2 \;\rightarrow\; S(CH_2CH_2Cl)_2 \;+\; S.$$

But a large part of the sulfur indicated in the equation as becoming free is, in fact, retained in solution in the resulting liquid, though more may come out of solution on storage, particularly at elevated temperatures.

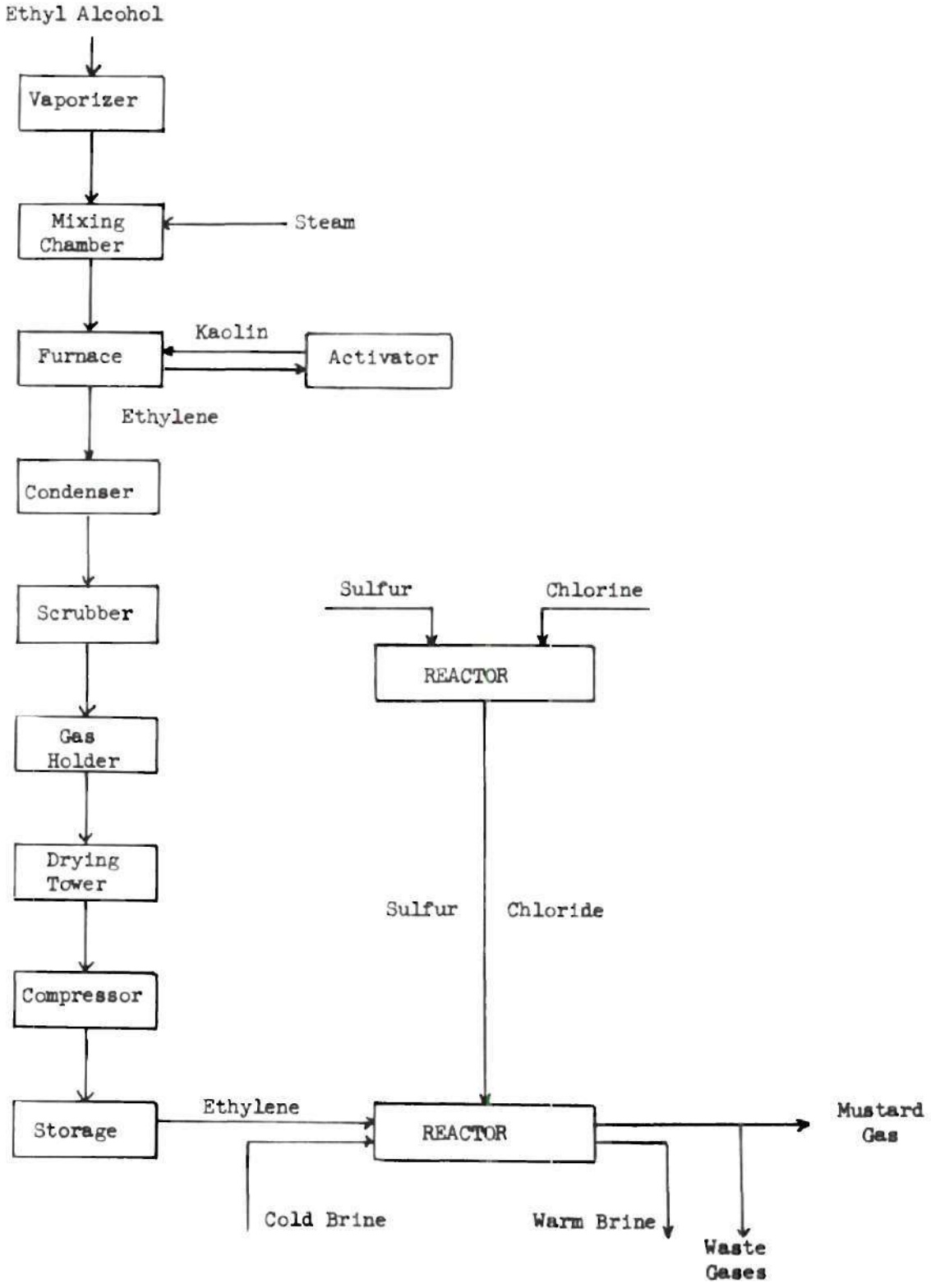


Figure 1. Levinstein Process. Flow Sheet.

The apparently capricious reappearance of sulfur has given trouble in manufacture and to control deposition of sulfur, a full knowledge of the nature of the solution is desirable. The problem is, in addition, one of great chemical interest.

The behavior of Levinstein mustard gas and the solubility of sulfur in β,β-dichloroethyl sulfide and related compounds rule out the possibility of the sulfur being retained in simple solution. The possibility of a so-called colloidal solution of sulfur appears to be ill-founded as no stable colloidal dispersion of sulfur in a liquid which is appreciably a solvent for sulfur is known.

A stable trisulfide was isolated by Mann, Pope and Vernon (11), and evidence that a stable disulfide is present was due to Foster, Harvey and Hands (12), but these alone cannot account for all the sulfur present.

Method of Separation of Constituent.--Sulfur is precipitated as a milky suspension which slowly crystallizes on standing, when Levinstein mustard gas is dissolved in excess of cold acetone. The amount of sulfur obtained in this case is only a small fraction of the whole, and is the sulfur present in true solution.

Thermal decomposition occurs when separation of the higher boiling fractions of Levinstein mustard gas is attempted by vacuum distillation. This was traced to the presence of a labile polysulfide which can be removed by a preliminary reflux with acetone. The resultant solution, after removal of the sulfur which is set free by this treatment can be distilled under reduced pressure.

The method used by Kinnear and Harley-Mason (12) involved the following stages:

(a) Preliminary distillation. This was a low temperature distillation giving a distillate consisting mainly of β,β-dichloroethyl sulfide, and an oily residue consisting mainly of trisulfide, a labile polysulfide and a small amount of the disulfide.

(b) Acetone reflux of the above residue to bring about deposition of sulfur from unstable compounds.

(c) Vacuum distillation of the acetone solution from stage b. After removal of sulfur to give disulfide and trisulfide fractions.

(d) Fractionation of the distillate from stage a, giving mono- and disulfide. The fractionating column used was constructed of twenty feet of one-inch-diameter glass tubing, coiled into a spiral, the whole being lugged with glass wool.

The details of the procedure are diagrammatically shown in Figure 2.

The composition of the sample was approximately the following:

β,β-dichlorodiethyl sulfide	61.4 per cent
β,β-dichlorodiethyl disulfide	4.3 per cent
β,β-dichlorodiethyl trisulfide	17.4 per cent
sulfur free and combined with trisulfide	10.7 per cent
tars and experimental losses	6.2 per cent.

Other Considerations about Composition.--Exhaustive hydrolysis of Levinstein mustard gas has been found to yield a residue which is thought to be a mixture of higher polysulfides. The pentasulfide has

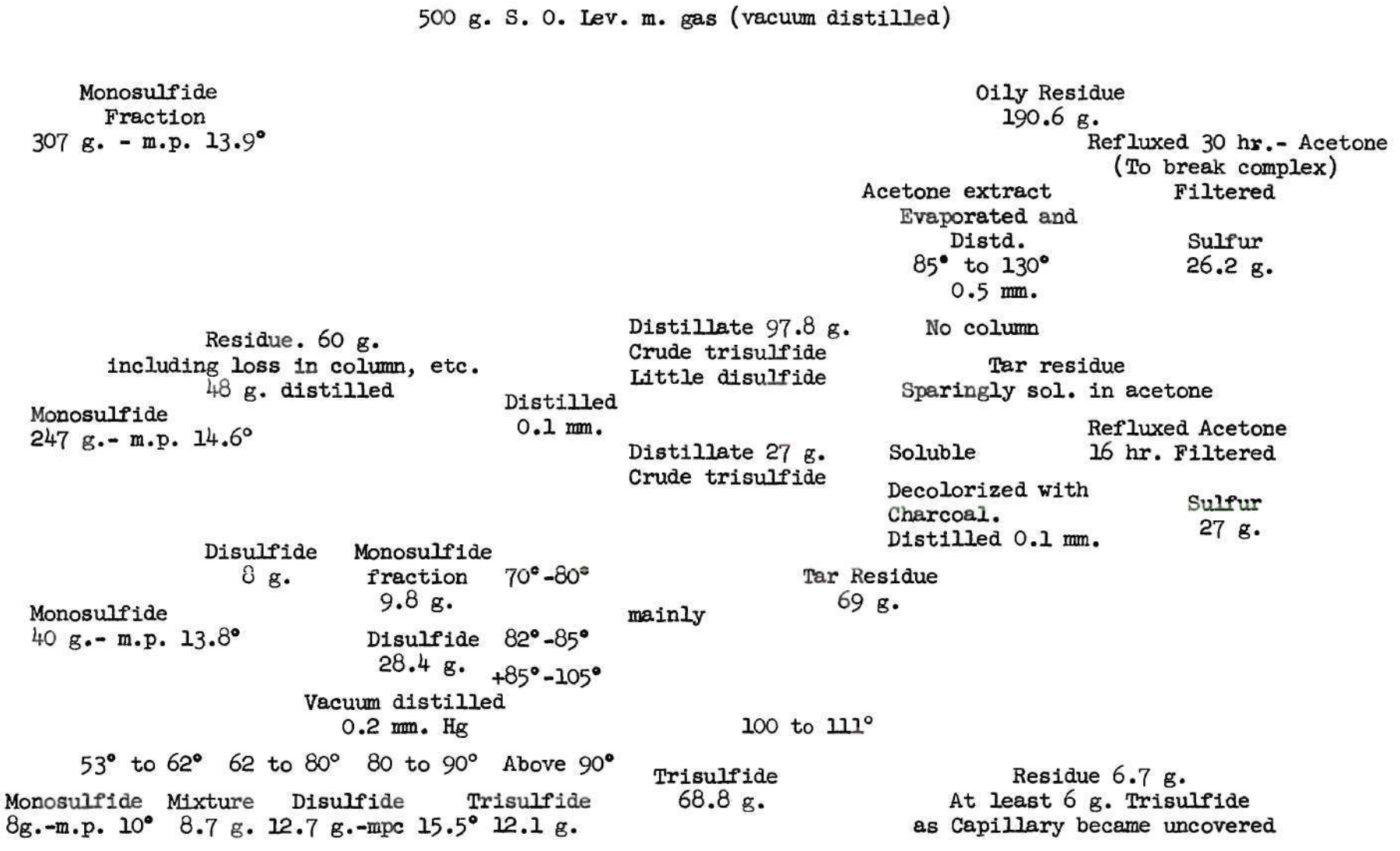


Figure 2. Diagram of Procedure for Separation of Constituent.

been obtained by subjecting the mixture to steam distillation and to stripping with Cellsolve or ammonia. The same compound has been made by sulfurization of the corresponding di and tri sulfides with sulfur and of the trisulfide with methyl tetrasulfide. The pentasulfide has been stripped to the trisulfide by ammonia in the presence of Cellsolve or ether and to the tetrasulfide by boiling acetone. Steam distillation of the pentasulfide was found to cause its degradation to the trisulfide. It has been concluded that both the disulfide and trisulfide possess the linear rather than the angular structure.

The disulfide, known to be linear, takes up an atom of sulfur only with difficulty. Then two additional atoms of sulfur may be added with comparative ease to produce the pentasulfide, degradation of which yields the trisulfide.

$$ClCH_2CH_2SSCH_2CH_2Cl + S \rightarrow ClCH_2CH_2SSSCH_2CH_2Cl$$

The structure of the higher polysulfides could be of the following type.

$$\begin{array}{c} S \\ S \\ ClCH_2CH_2SSSCH_2CH_2Cl \\ S \\ S \end{array}$$

This type of structure is in accord with the facts that sulfur atoms are naturally chain-forming and that the polysulfides above the pentasulfide readily lose sulfur.

The gradual conversion of plastic sulfur, S_μ, which is supposed to consist of long sulfur chains to the stable λ-sulfur is accelerated by ammonia. This may be related to the observed stripping of higher polysulfides to the pentasulfide by ammonia.

Reports of the existence of bis(2-chloroethyl) disulfide in Levinstein mustard gas are in disagreement (12). This is not at all surprising due to the tendency of the higher polysulfides to decompose under the influence of heat to give the trisulfide (and free sulfur) which is degraded to the disulfide by distillation.

It is apparent that any reliable method for determining the amount of disulfide present in the Levinstein mustard gas must involve only mild conditions.

It was observed that the refractive indices of mixtures of the disulfide and pentasulfide, and of the disulfide and trisulfide followed a linear relationship with respect to the mole fraction of the constituent. Thus, measurement of the refractive indices of the stripped residue from the hydrolysis of Levinstein mustard gas and of the steam distillated of the residue, indicated the presence of one to two per cent of the disulfide in the crude mustard gas. This value is in good agreement with that obtained by MacInnes and Beleher (10) by analysis of a fraction from the molecular distillation of Levinstein mustard gas. These considerations explain some of the results of the method of separation of constituent described.

C. Mechanism of Formation

The following mechanism has been suggested by Fuson, Foster and Lipscomb (10) and accounts satisfactorily for the composition of mustard gas obtained by the Levinstein process.

In 1920 Conant, Hartshorn and Richardson (13), postulated a mechanism for the formation of mustard gas from ethylene and sulfur monochloride and dichloride. From the evidence then available, they assumed that 2-chloroethylsulfenyl chloride was an intermediate product in the process

$$CH_2{=}CH_2 \xrightarrow[S_2Cl_2]{SCl_2 \text{ or}} ClCH_2CH_2SCl \xrightarrow{CH_2=CH_2} (ClCH_2CH_2)_2S.$$

This theory has been substantiated by the isolation of 2-chloroethylsulfenyl chloride (pure) and by its reaction with ethylene to produce β,β-dichloroethyl sulfide, and also more recently, evidence that 2-chloroethyl sulfenyl chloride is an intermediate has been obtained by using an equimolecular mixture of ethylene and cyclohexene in the Levinstein process, instead of ethylene alone. β,β-dichloroethyl sulfide, bis (2-chlorocyclohexyl) sulfide and 2-chlorocyclohexyl-2-chloroethyl sulfide were obtained.

In a similar way an equimolar mixture of ethylene and cyclohexene was passed into a solution of sulfur dichloride in mustard gas. The same three products were obtained, demonstrating that the reaction of ethylene with sulfur dichloride proceeds in two steps and involves the intermediate formation of 2-chloroethyl sulfenyl chloride.

Any mechanism which is to account for the formation of Levinstein mustard gas must also provide a satisfactory explanation for the

formation of polysulfides desired from the linear trisulfide, as well as the virtual absence of the disulfide and of free sulfur. The following mechanism appears to fulfill these requirements.

Although sulfur monochloride may react only as such with ethylene, there is chemical and physical evidence to support the assumption that it may undergo disproportionation to form sulfur dichloride and sulfur tritadichloride.

$$2S_2Cl_2 \rightleftarrows SCl_2 + S_3Cl_2 \qquad (a)$$

In the Levinstein process, accordingly, the ethylene may react with the dichloride (b); the monochloride (c) or the tritadichloride (d).

$$2C_2H_4 + SCl_2 \rightarrow ClCH_2CH_2SCH_2CH_2Cl \qquad (b)$$

$$2C_2H_4 + S_2Cl_2 \rightarrow ClCH_2CH_2SSCH_2CH_2Cl \qquad (c)$$

$$2C_2H_4 + S_3Cl_2 \rightarrow ClCH_2CH_2SSSCH_2CH_2Cl \qquad (d)$$

If higher polythiosulfur chlorides, such as S_4Cl_2, were present they might condense in a manner analogous to that represented by equation (d).

The reaction of sulfur dichloride with ethylene is known to be very rapid. Accordingly, the excess of ethylene which is always present should serve to keep the concentration of sulfur dichloride at a very low value, thus promoting the displacement of the equilibrium (a) to the right and increasing the rate of formation of tritadichloride. This would

bring about a corresponding decrease in the amount of sulfur monochloride which could react with ethylene to produce disulfide (b).

However, it is to be expected that the reaction of ethylene with sulfur monochloride should proceed at least as rapidly as with sulfur tritadichloride (c and d). Therefore the only way to account for the virtual absence of bis (2-chloroethyl) disulfide in Levinstein mustard gas is to assume that the disulfide is attacked rapidly by sulfur monochloride.

Higher polysulfides are known to form a large fraction of the crude reaction product; therefore these compounds as well as the disulfide, undoubtedly are in contact with the sulfur chlorides during the course of Levinstein process. In an attempt to determine the results of such contest the polysulfides were subjected to the action of sulfur chlorides. It was found in such experiments that disulfide is attacked by sulfur monochloride in this way (10):

$$ClCH_2CH_2SSCH_2CH_2Cl + 3S_2Cl_2 \rightarrow 2ClCH_2CH_2SCl + 2S_3Cl_2. \quad (e)$$

The formation of sulfur tritadichloride as a product of this reaction obviates the necessity of assuming the disproportionation of sulfur monochloride (a), to account for the formation of bis (2-chloroethyl) trisulfide. However, that is still considered a definite possibility. The trisulfide (formed in d) is known to be sulfurized readily at 30-35°C by sulfur monochloride to higher polysulfides (f; g; h) and sulfur dichloride is the other product of the reaction. It reacts immediately with ethylene to produce mustard gas.

$$ClCH_2CH_2SSSCH_2CH_2Cl + S_2Cl_2 \rightarrow (ClCH_2CH_2)_2S_4 + SCl_2 \qquad (f)$$

$$(ClCH_2CH_2)_2S_4 + S_2Cl_2 \rightarrow (ClCH_2CH_2)_2S_5 + SCl_2 \qquad (g)$$

$$(ClCH_2CH_2)_2S_5 + S_2Cl_2 \rightarrow (ClCH_2CH_2)_2S_6 + SCl_2 \qquad (h)$$

etc.

Because sulfur dichloride is generated in the reaction mixture only as a product of other reactions, and because an excess of ethylene is always present, the concentration of sulfur dichloride can never be very great. For this reason overchlorination is not a serious problem as in the processes involving sulfur dichloride directly.

The net result of this series of reactions is the production of a mixture of β,β-dichloroethyl sulfide and the corresponding polysulfides.

$$2XC_2H_4 + XS_2Cl_2 \rightarrow (X - 1)ClCH_2CH_2SCH_2CH_2Cl + (ClCH_2CH_2)_2S_{X+1}$$

The composition of the polysulfide as well as its concentration in fresh Levinstein mustard gas depends on the conditions under which the reaction was run, especially on the temperature, degree of agitation, amount of feed charge, rate of addition of ethylene, and very likely many other factors, such as previous history of the sulfur monochloride, have an important effect. So long, however, as there is no sulfur precipitated during the reaction (the problem in the first industrial attempts), there must be, according to the general equation above, a definite relationship between the composition of the polysulfide and its concentration. Empirically, one sulfur atom is produced each time a

molecule of β,β-dichloroethyl sulfide is formed and this sulfur must all be present as polysulfides. The higher the sulfur content of the polysulfide, the lower must be its concentration. Table 2, which follows, illustrates this relationship. The monosulfide-polysulfide ratios tabulated are those which would be required to satisfy the general equation. The table lists other properties, based on theory, which the original mixtures should have. Also included are the calculated pentasulfide-monosulfide ratios in the products obtained by stripping or aging the original mixtures.

The theoretical values which appear in the table are in excellent agreement with the great quantity of experimental data.

D. The Effect of Temperature on the Levinstein Process

The mechanism which has just been outlined is further supported by results obtained in a study of the effect of temperature on the reaction. The amount of impurities (polysulfides) in the Levinstein mustard gas depends on the rate of formation of the trisulfide and on the rate of its sulfurization by sulfur monochloride.

The increase in the rate of the reactions with increase in temperature is partially offset for those reactions involving ethylene, because of the decreased solubility, and therefore concentration of ethylene in the warmer solvent. Thus the sulfurization reactions (f; g; and h) would be expected to proceed relatively more rapidly than the other reactions, which depend upon the concentration of ethylene. Each time an atom of sulfur is added to a polysulfide molecule, a molecule of β,β-dichloroethyl sulfide must be formed concurrently in order to preserve the stoichiometric relationship.

Table 2. Relationship between Composition and Properties of Polysulfides

Polysulfide-Monosulfide Mixtures Which Satisfy the General Equation						Pentasulfide-Monosulfide Mixtures Produced by Stripping
Mixture	Mole Ratio	Mole Per Cent	Weight Per Cent	Calc'd F.P.	Weight Per Cent Strippable Sulfur	Weight Per Cent
Monosulfide	3	75	62.5	5.6	0	62.5
Pentasulfide	1	25	37.5			37.5
Monosulfide	4	80	66.8	7.2	3.4	69.0
Hexasulfide	1	20	33.2			31.0
Monosulfide	5	83.3	69.5	8.5	5.5	73.6
Heptasulfide	1	16.7	30.5			26.4
Monosulfide	6	85.7	71.5	9.1	7.2	76.9
Octasulfide	1	14.3	28.5			23.1
Monosulfide	7	87.5	72.9	9.7	8.4	79.6
Nonasulfide	1	12.5	27.1			20.4
Monosulfide	8	88.9	74.1	10.4	9.3	81.7
Decasulfide	1	11.1	25.9			18.3

Thus at elevated temperatures the reaction between ethylene and sulfur monochloride might be expected to proceed more rapidly and to produce a greater yield of monosulfide at the expense of the polysulfide fraction.

However, the polysulfides which were formed would have a higher sulfur content than those produced at low reaction temperatures. These considerations have been borne out by the following experimental observations (10).

When the sulfur monochloride-ethylene reaction was carried out at 60°C the reaction proceeded rapidly to give high yields (80 per cent) of β,β-dichloroethyl sulfide and large amounts of sulfur free. If the rate of sulfurization was high, then as fast as the trisulfide was produced it was sulfurized by sulfur monochloride to higher polysulfides. Since a molecule of β,β-dichloroethyl sulfide was produced each time a sulfur atom was added to a polysulfide molecule, the amount of β,β-dichloroethyl sulfide was large also in this case. The higher polysulfides produced are unstable at elevated temperatures and deposit sulfur readily.

When run at 35°C, as in the Levinstein process, the reaction proceeded somewhat more slowly, the yield of β,β-dichloroethyl sulfide was less (70 per cent) and sulfur was observed to precipitate only after the product was allowed to stand for several weeks. Here the rate of sulfurization was moderate and the polysulfides formed were of lower molecular weight and consequently more stable.

When the reaction was carried out at 20°C the yield of β,β-dichloroethyl sulfide was only 61 per cent and the polysulfide portion

made up 39 per cent of the total product. The polysulfide fraction proved to be nearly pure pentasulfide and contained only traces of higher polysulfides. Apparently the rate of sulfurization was low and the yield of β,β-dichloroethyl sulfide correspondingly low. If no sulfurization took place the yield of the sulfide would be only 50 mole per cent (41.6 per cent in weight) and the trisulfide would be the other product. It is likely that the latter is sulfurized to pentasulfide so readily that it would not be possible to carry out the reaction to produce polysulfides lower than the pentasulfide. This contention seems to be borne out by the results obtained when the reaction was run at a still lower temperature (12°C). The polysulfide obtained had an average composition higher than the pentasulfide.

Through the study of the composition, mode of formation and manufacture it is possible to determine the best conditions to run the production of mustard gas using the Levinstein process from the viewpoint of temperature, degree of agitation, amount of feed charge, rate of addition of ethylene and purity and previous history of raw materials.

To obtain a guide for the calculation necessary for the proper design and layout of a pilot plant, there is a very useful article by K. B. Guinan published in The Industrial Chemist, which fulfills all the theoretical requirements except the conditions in which the reaction must be run (14).

CHAPTER VI

PURIFICATION OF MUSTARD GAS

The Levinstein process, the simplest and least expensive method for the manufacture of mustard gas, involves the direct reaction of ethylene with sulfur monochloride. A product containing approximately 70 per cent of β,β-dichloroethyl sulfide is obtained.

Due to the fact that by increasing the percentage of β,β-dichloroethyl sulfide it is possible to obtain a product with less odor and a greater blistering action (important military properties) it is desirable to purify the Levinstein mustard gas if the cost is not increased considerably.

A. Solvent Extraction of Crude Mustard Gas

In an attempt to purify the crude material a solvent extraction process was extensively investigated in The Chemical Warfare Laboratories, Ottawa. The report of this work was made by R. Mungen (15).

The samples of crude mustard gas used in this investigation were dark brown in color, contained approximately 70 per cent of β,β-dichloroethyl sulfide and had melting points ranging from 5.9°C to 6.5°C.

In any purification process it would be desirable to avoid decomposition due to excess heating or chemical reaction.

Studies of the solubility of crude mustard gas in a large number of organic solvents were undertaken to find a suitable solvent for the extraction of β,β-dichloroethyl sulfide. The majority of these liquids

were completely miscible with the crude material at ordinary temperatures. Others reacted with it, in many cases precipitating sulfur. It was concluded that hydrocarbons in the pentane boiling point were the most suitable solvents for the purification of crude mustard gas.

Extraction Experiments. Single Batch Extraction.--Initial extraction experiments were carried out by shaking crude mustard gas with solvent in a separatory funnel. After separation the solvent layer was removed and analyzed.

Crude material was extracted with equal volume of petroleum ether (boiling range 30° to 60°C). When the solvent was removed from the resulting solvent layer, a product of approximately 80 per cent purity was obtained. From this it seems that a partial purification can be made using solvent extraction.

Continuous Extraction.--A small glass column was built to study continuous counter-current extraction of β,β-dichloroethyl sulfide from the crude material. The specific gravity of the mustard gas was 1.3 and that of the solvent 0.65. The flow rate of the crude mustard gas feed was 10 ml. per minute, and the solvent flow rate was varied to give solvent/feed ratio of 5/1. Using ratio greater than this increased the yield but reduced the purity of the product.

From this result it was apparent that products of high percentage purity with good recovery could be obtained only from a complete extraction system including rectification. More complete equilibrium data were required to continue work on a pilot plant scale.

The solvent chosen from a consideration of cost, availability and solvent properties was Skellysolve A, a mixture of pentanes with a

boiling range of 93° to 95°F, 60 per cent boiling at 94°F. For the equilibrium studies the crude material is considered to be a two-component system, β,β-dichloroethyl sulfide (H) and impurities (I), and the data are based on the three-component system.

In order to obtain a wide range of points on the equilibrium curve, it was necessary to have Levinstein mustard gas samples of a wide range of purities. Samples rich in H were obtained by adding extracted material to nearly pure H or vice-versa. Samples low in H and high in I content were obtained by continued re-extraction of the crude material.

The method of treating the equilibrium data was that given by Maloney (16). The equilibrium data were used to calculate the operational variables of the extraction column. From the equilibrium data it is apparent that it is not possible to obtain 100 per cent pure β,β-dichloroethyl sulfide from the crude mustard gas using a solvent extraction process with pentane fractions as the solvent. The maximum purity that can be expected with a reasonable number of contact units and practical reflux ratio is about 92.5 per cent.

From the equilibrium data and the small column extractions it was possible to estimate the height of a theoretical contact unit (H.T.C.U.). This height was found to vary markedly with flow rates but for practical flows was from three to five feet.

Pilot Plant.--A flow diagram of the pilot plant is shown schematically in Figure 3. The extraction column is of standard four-inch iron pipe assembled with standard coupling. The packing is half-inch glass raschig rings. The column is wound with resistance wire over its entire length and insulated with rock wool to permit temperature regulations. The crude feed enters at the 12-foot level.

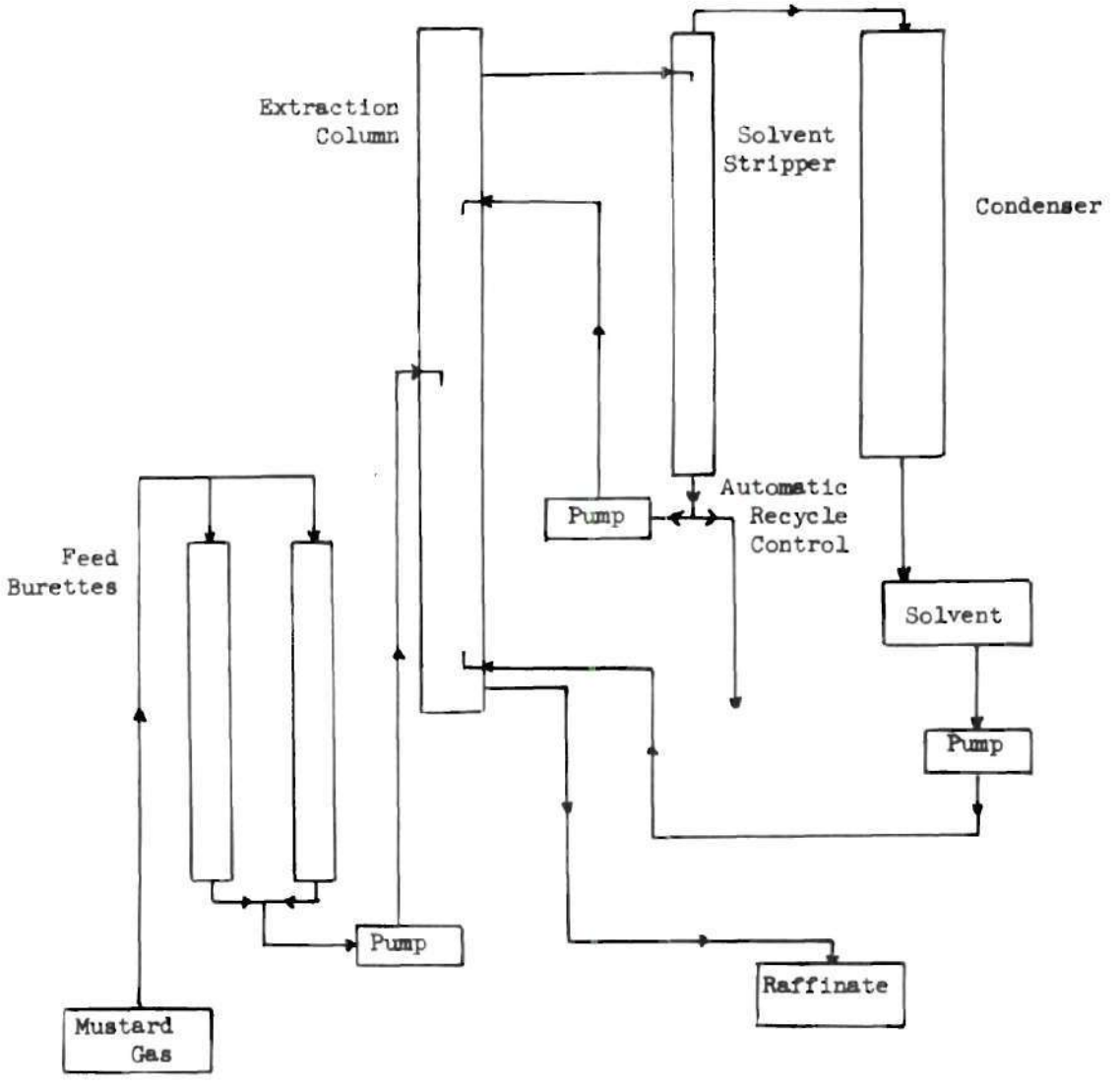


Figure 3. Flow Diagram. Pilot Plant for Solvent Extraction

The solvent stripper is made of 14-gauge 18-8 stainless steel 10 feet long and two inches in diameter. It is fitted with a steam jacket operated at 5 to 10 lb. steam pressure. The product cooler is a water-jacketed 18-8 stainless steel tube 3/8-inch I. P. S., six feet in length. The solvent condenser is of the ordinary tube variety made of mild steel.

The condenser is five feet long, six inches in diameter and had 17-1/4 I. P. S. tubes. The cooling water flows through the tubes.

The feed pump is a Hills-McCanna proportionating pump. The solvent reflux pumps are rotary gear pumps. The recycle regulator is operated magnetically on a time ratio.

The feed burettes are made of three-inch I. P. S. mild steel four feet long, fitted with full-length sight gauges. They are calibrated in 100-ml. units and serve to adjust the feed rate of the pump. The two burettes are arranged so that one could be filled while the other supplies the pump with feed liquid. The line from the feed drum to the burettes passes through a glass wool filter to prevent sulfur from reaching the pump and interfering with the valve operation.

The product and raffinate receivers are 45 gallon drums fitted with sight gauges. The solvent receiver and reflux receiver are smaller mild steel drums also fitted with sight gauges.

The lines and fittings are all of 1/4-inch, 3/8-inch and 1/2-inch I. P. S. mild steel. The globe valves are of iron and the solvent rotameter is a standard Schutte-Koerting model.

Operation.--To start operating crude mustard gas is fed into the column until it appears in the sight gauge (12 feet from bottom of column). The solvent is then pumped in at a slow rate. As the interface begins to rise the solvent rate is increased and the feed rate reduced.

The flow rates are gradually adjusted to desired values and the interface kept at a definite level by adjusting the rate of removal of raffinate. Continuous operation is automatic, requiring minor adjustments to flow rates and temperatures. There is no trouble from plugging of lines by sulfur deposits. The raffinate flows freely. Plant operational data are shown in Table 3.

Results of Continuous Extraction Runs.--The continuous extraction runs demonstrated the effect of varying flow rates, solvent dosage and reflux ratio. The temperature of the column was kept at 25°C for all runs. Since the reflux enters at the top of the column a certain fraction of the enriching section is required for mixing. At the bottom the solvent must mix with raffinate before equilibrium is approached and a portion of the stripping was used for this purpose. The portion of the column used for mixing was unknown and as a result, errors are introduced into calculation of H. T. C. U.

The time required to reach equilibrium was different for the stripping section as compared to the enriching section.

A product of constant melting point would appear in four hours, but the composition of the raffinate would not agree with its calculated value for as long as 24 hours. The product containing 4.0 to 4.5 per cent solvent, varied in color from pale yellow to almost colorless, depending on the purity. The iron and acid contents were negligible.

Table 3. Plant Operational Data. Solvent Extraction.

Run Number		2	6	8	9	10	14	17[1]
Duration of run (hr.)		21	43	29	24	31	68	23
Reflux ratio		4/1	6/1	6/1	6/1	8/1	8/1	3.5/1
Feed rate, ml./min.		100	30	50	70	40	43	50
Feed rate, lb./hr./sq. ft.		205.7	61.7	102.9	143.9	82.3	88.4	102.9
Solvent rate, ml./min.		2000	670	910	1275	910	910	1025
Solvent rate, lb./hr./sq. ft.		1881	630	856	1200	856	856	965
Solvent dosage, lb. solvent/lb. feed		9.2	10.2	8.3	8.35	10.4	9.7	9.4
Crude Mustard Feed	M.P., °C	6.1	6.1	6.1	6.5	6.5	5.9	6.0
	Wt. % H Content by Distillation	70.1	70.1	70.1	70.2	70.2	69.9	70.0
Extract product on solvent free basis	% Total recovery	73.6	69.8	61.2	58.8	61.0	55.2	80.5
	% H recovery	87.2	86.0	77.7	74.4	80.6	72.2	94.2
	M.P., °C	9.0	9.9	10.9	10.4	12.0	11.6	8.7
	Wt. % H Content by Distillation	83.1	86.0	89.1	87.5	92.5	91.3	82.2
% Solvent in Product		4.3	4.4	4.2	4.4	4.1	4.6	4.3
Raffinate on solvent free basis	% Total feed	25.8	32.0	39.4	40.2	38.2	46.3	20.0
	Wt. % H content	32.9	29.8	38.7	49.3	39.2	45.2	19.5
% Solvent in raffinate		5.2	4.0	5.2	6.3	5.2	5.4	3.1
T. C. U. (enriching)		1.5	2.2	4.3	3.2	17.0	8.3	1.2
T. C. U. (stripping)		2.0	2.0	2.0	1.5	2.0	1.8	2.8
H. T. C. U. (enriching)		16	10.9	5.6	7.5	1.4	2.9	10.0
H. T. C. U. (stripping)		6	6	6	8	6	6.7	8.6

[1] Stripping section 24 ft.
Enriching section 12 ft.
T. C. U. theoretical contact unit

There was a slight deposit of sulfur from extract products of high purity. Occasionally sulfur precipitated from the product in the product cooler, but never in sufficient quantities to cause trouble. This sulfur was most probably carried over by the solvent when high reflux ratios were used, and remained in the product when the solvent was removed. Another source of sulfur would be the polysulfides, which may partially decompose on removal of the solvent at 100°C.

Summary.--Pilot plant operation has demonstrated that a maximum purity of approximately 92.5 per cent can be obtained under extreme conditions of reflux, as predicted by the equilibrium data.

An examination of Table 3 shows that only by accepting low yields and reflux ratios of 8/1 was it possible to obtain a product approaching maximum purity (Runs 10 and 14). This indicates that the stripping section was of insufficient length to produce good stripping. In Run 17 when the stripping section was 24 feet long the yield of β,β-dichloroethyl was 94 per cent. The column was not long enough to give a product of maximum purity together with good yields.

It is to be noted that the H. T. C. U. stripping seems to be much less affected by flow rates than the H. T. C. U. in the enriching section. Under favorable conditions (Runs 10 and 14) the H. T. C. U. enriching is about three feet, while the H. T. C. U. stripping is from six to eight feet in all the runs.

The complete assessment of the product depends on many factors, including storage trials in weapons.

B. Vacuum Distillation

Mustard gas boils at 217°C at atmospheric pressure, but with considerable decomposition. It may be distilled under a high vacuum, but it is important to limit the time of exposure of a given portion of the liquid to the necessary high temperature to the shortest possible time.

The apparatus herein described was constructed in the American University Experiment Station (17), and it is mentioned in this work as an example of how to conduct such operation in a semi-pilot-plant scale. The construction and operation of the apparatus will be understood by reference to the drawing (Figure 4).

The stock bottle for the crude mustard gas stand on a platform scale to facilitate determining the rate of consumption. The rate of flow is regulated and observed through a sight-glass. The liquid then enters a pre-heating coil consisting of 50 feet of half-inch pipe in a bath of hot oil. This oil is kept at a predetermined temperature by means of valves in the oil circulating system (not shown).

The gas separator consists of a cylinder four inches in diameter and 12 inches deep surrounded by a jacket with hot oil. The liquid enters at the side, three inches above the bottom and is withdrawn at the bottom. A gauge glass is provided to show the level of the liquid in the chamber. This level should be kept constant. The gas separated in the upper part of the chamber and is led off into the scrubbing and condensing system.

A regular flow of liquid through the pre-heater is maintained by controlling the valve on the vacuum line beyond the scrubbing system so

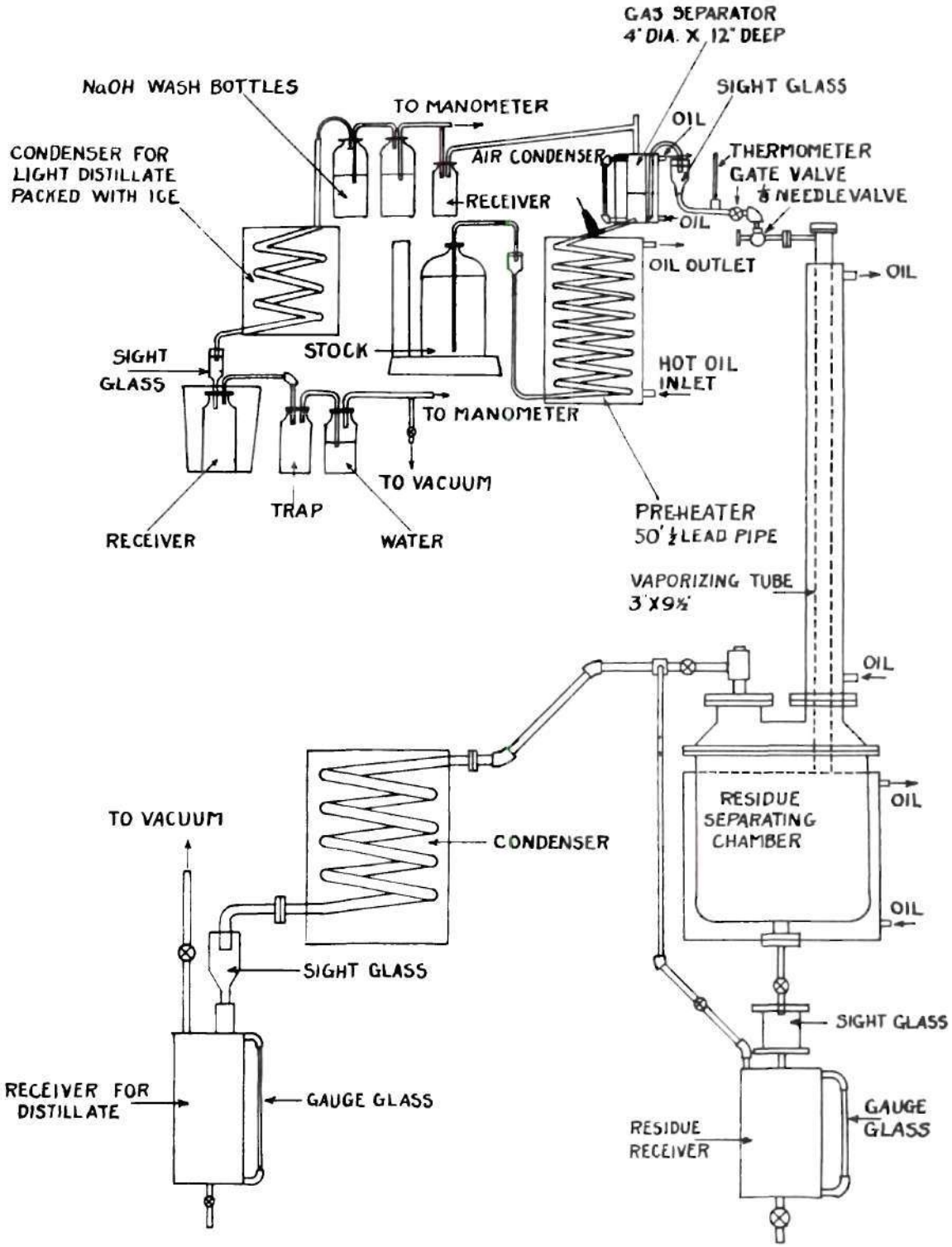


Figure 4. Vacuum Distillation. Pilot Plant.

that the manometer on the gas separator registers 10 cm. of mercury vacuum. This might be automatic. The liquid is aspirated from the separator in the still, flowing through a sight glass and two valves (the first to control starting and stopping and the second a needle valve to regulate the flow). It enters the vaporizing tube through a 3/8-inch pipe bent to give a horizontal tangential discharge against the wall. This tube is a three-inch iron pipe, 9-1/2 feet long, surrounded by a jacket through which hot oil is circulated. The liquid flows as a thin film down the walls of this tube and the vapors formed, together with the unevaporated residue enter the large separating chamber below. This residue is continuously drawn off into the residue receiver (while the vapor passes on to the condenser) and is collected as a liquid in the distillated receiver. Both receivers are provided with sight glasses to observe the flow and gauge glasses to show the volume.

The operation of this apparatus could easily be made continuous by installing duplicate receivers and reservoirs for stock.

Results of Experimental Runs.--Several runs were made to determine the most satisfactory conditions of temperature and rate of feed. The best runs gave results as follows:

Average temperatures

Bath of pre-heater and gas separator	150°C
Bath around vaporizing tube	183°C
Bath around residue separator	150°C
Mustard gas entering vaporizing tube	147°C
Mustard gas vapor entering condenser	136°C

Average vacuum (absolute pressure in mm. of mercury)	60
Average rate of feed, pounds per minute	0.95
Average rate of condensation, pounds per minute	0.57
Per cent of charge as distillate	53.5
Purity of distillate	92.5
Per cent of charge as residue	40.6
Purity of charge	81.5
Per cent of original mustard gas remaining in residue	32.0

Other runs were made under different conditions, with the following conclusions:

(1) Increasing the temperature at any point increased the decomposition, lowering the vacuum and yield.

(2) Lowering the temperature at any point reduced the yield.

(3) Increasing the rate of feed did not increase the rate of distillation and reduced the per cent yield.

(4) Reducing the rate of feed increased the per cent yield, but not proportionally and reduced the rate of distillation.

There was found to be a considerable amount of material vaporized in the pre-heater and separated in the gas separator. A typical run gave results, expressed in per cent of original crude mustard gas, as follows:

Condensate, air condenser	1.8
Absorbed in alkali	2.3 (Mostly HCl)
Light condensate	1.4

If the temperature of the pre-heater was raised appreciably above 150°C there was much light material given off and the liquid delivered to the still was lower in temperature, due to decomposition with absorption of heat. When material that had once passed through the pre-heater was again put through at the same temperature, there was practically no further evolution of gas. This would indicate that the amount first obtained originally existed in the crude material.

CHAPTER VII

DETECTION AND DETERMINATION OF MUSTARD GAS

A. Quantitative Determination of Mustard Gas in Industrial Products

The usual procedure for the estimation of β,β-dichloroethyl sulfide in a sample is to distill a known volume under diminished pressure and to collect the fraction boiling at 125 to 130°C at 40 mm. of mercury. This product is fairly pure and the volume obtained affords an approximation of the purity of the crude product. This procedure involves personal risks and gives no accurate figure for the absolute percentage of β,β-dichloroethyl sulfide, as the latter fraction also contains impurities (higher chlorinates compounds).

Hollely's Volumetric Method.--This method depends upon the fact that the sulfide forms a definite double salt with cuprous chloride of the following constitution

$$S\begin{matrix}CH_2CH_2Cl \\ CH_2CH_2Cl\end{matrix}{}_2 \cdot Cu_2Cl_2$$

As the higher chlorinated compounds do not react with cuprous chloride, the method is applicable for the absolute estimation of the sulfide (18).

Grignard, Rivat and Scatchard Method.--This method is based on the fact that when a 10 per cent solution of β,β-dichloroethyl sulfide in glacial acetic acid is heated with a 67 per cent solution of hydriodic acid at

50-70°C, a yellowish oil is deposited which solidifies on cooling to a crystalline mass of diiodoethyl sulfide melting at 62°C, and on the determination of the quantity of HI which has not reacted.

$$S(CH_2CH_2Cl)_2 + HI \rightarrow S(CH_2CH_2I)_2 + 2HCl.$$

There are no indications in the literature of the accuracy of the results obtained by this method (19).

B. Quantitative Determination of Mustard Gas in Air

Nephelometric Method of Yablick, Perrot and Furman.--This method determines quantitatively the presence of traces of β,β-dichloroethyl sulfide in the air by reducing a one per cent solution of selenious acid in dilute sulfuric acid by means of the sulfide vapor to an orange-red suspension of selenium. Amounts of the sulfide as small as 0.005 to 0.001 mg. can be detected in this way. The amount of suspension produced is nearly directly proportional to the amount of the sulfide present, and 0.10 to 0.01 mg. can be established nephelometrically with a fair degree of accuracy (±0.005 mg).

This method is remarkably free from the necessity for extreme purity of the original solutions, cleanliness of glassware, etc., but the selenious acid reagent is not specific to β,β-dichloroethyl sulfide; for arsine and the substituted arsines and several other toxic gases react with it vigorously (20).

Method of Maxim.--In this method the sulfur of the sulfide is oxidized by means of potassium permanganate, then passing the gas into barium chloride solution containing hydrogen peroxide. The barium sulfate precipitated is washed, dried and weighed (21).

Potentiometric Method of Hopkins.--Hopkins (8) introduced a new rapid method whose principle is dependent upon the increase in the hydrogen ion concentration. It consists in hydrolyzing the β,β-dichloroethyl sulfide with water at 35°C and determining the hydrogen ion concentration of the solution obtained by a potentiometric method.

C. Summary

The following reagents have been proposed for the detection of β,β-dichloroethyl sulfide (1).

Potassium Permanganate.--A 0.003 per cent solution of potassium permanganate acidified with a few drops of sulfuric acid is decolorized by air containing mustard gas vapor. The minimum quantity of the sulfide producing a distinct color change is about 0.15 mg.

Congo Red Paper.--Detection using this paper depends on the formation of hydrochloric acid by decomposition of β,β-dichloroethyl sulfide with sulfuric acid.

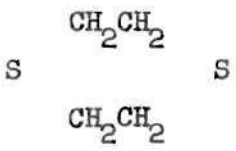
β-Naphthol.--On passing mustard gas vapors through an alcoholic and strongly alkaline solution of β-naphthol a turbidity is produced which slowly settles. With this reagent as little as 0.06 mg. of mustard gas may be recognized.

Potassium Mercuri-Iodide.--On passing air containing mustard gas vapor through an aqueous solution of potassium mercuri-iodide at 40-45°C, a whitish-yellow precipitate separates. The limit of sensitivity is 0.03 mg.

Hydrogen Peroxide.--When air containing mustard gas is passed through a solution containing 30 per cent by volume of hydrogen peroxide in acetic acid, colorless acicular crystals are formed, first in the air inlet and then in the liquid.

Sodium Iodoplatinate Paper.--This test paper changes from its original pink color to violet by the action of β,β-dichloroethyl sulfide. Sensitivity 0.02 mg.

Sodium Monosulfide.--On passing air containing mustard gas through a concentrated solution of sodium monosulfide, a white turbidity is produced due to the formation of diethylene disulfide of the following structure.



Schroter's Reagent.--The use of this reagent is based on the property of β,β-dichloroethyl sulfide of forming additive compounds with gold and palladium chlorides.

On treating an aqueous solution containing 0.1 per cent gold chloride or 0.05 per cent palladium chloride with mustard gas a turbidity of colloidal type quickly forms, and if the quantity of the sulfide is large yellowish-red oily droplets are produced.

This reaction may also be carried out on filter paper. In this case a reddish-brown stain is formed with a 10 per cent gold chloride and a yellow stain with a 0.2 per cent palladium chloride solution.

An apparatus has been designed for detecting the presence of mustard gas in a sample of air by this reaction.

The sensitivity is 12 mg. of the sulfide per cubic meter of air.

CHAPTER VIII

LABORATORY PREPARATION OF MUSTARD GAS

Gomberg Method.--Mustard gas can conveniently be prepared by warming β,β-dihydroxyl ethyl sulfide (commercially available Eastman Kodak NOT 1224) with concentrated hydrochloric acid (1).

$$(CH_2CH_2OH)_2S + HCl \rightarrow (CH_2CH_2Cl)_2S + 2H_2O$$

In practice it is convenient to use a large excess of acid in order to drive the reaction to completion. 250 grams of β,β-dihydroxyl ethyl sulfide are dissolved in 400 ml. of concentrated hydrochloric acid, and the solution is warmed to 60 to 75°C for 30 minutes. A longer time will do no harm. A heavy yellow oil separates as the lower layer. The aqueous layer is then poured off, the oil being washed rapidly with a little distilled water and transferred to a storage bottle. This preparation should be carried out in a hood with good ventilation, the aqueous layer poured into a cream of bleaching powder to destroy any mustard gas, and the hands washed promptly with bleaching powder to remove any mustard gas absorbed from the gas phase.

It is convenient to use cork stoppers covered with metal foil, since mustard is readily absorbed by rubber. In fact rubber tubing will completely remove mustard gas from an air stream, only to give it off later when the tube is more or less saturated.

Guthrie's Method.--Mustard gas may be easily prepared by following Guthrie's original method (1) of bubbling ethylene through sulfur monochloride.

$$2C_2H_4 + S_2Cl_2 \rightarrow (CH_2CH_2Cl)_2S + S$$

The reaction may be carried out in a three-necked round bottomed flask fitted with a dropping funnel, a mechanism stirrer and an inlet tube for admitting ethylene. Ethylene is first dried by passing through a tower of concentrated sulfuric acid and one of glass wool and then admitted to the round-bottomed flask, which contains 20 grams of sulfur monochloride introduced through the dropping funnel. During the passage of ethylene a further 30 grams of sulfur monochloride are added from the funnel. The flask in water bath is heated on an electric hot plate, and a stream of cold water is arranged to flow over the flask, in order to maintain a temperature of not over 35°C. The passage of ethylene is continued until all the sulfur monochloride has been used up. This is determined by treating a little sodium iodide solution on filter paper with a drop of the reaction mixture. A brown stain indicates incomplete reaction.

At the end of the reaction the product may be distilled under reduced pressure, the fraction passing over between 106 and 108°C being collected (15 mm. of mercury).

Preparation of Highly Purified Mustard Gas.--Despite its low melting point crystallization from a suitable solvent seems to be the most promising method to purify mustard gas (22). It was found that crystallization of the compound occurred readily from dilute solution in petroleum ether

or absolute ethanol if the solution is cooled to approximately -75°C. In this way purification is readily effected.

CHAPTER IX

CONCLUSIONS

Compared with the properties of the ideal defensive gas, as set forth in pages 3 - 13, mustard gas meets the following requirements.

Physical Properties.--

1. Volatility is low. The maximum field concentration is 3.06 mg./l.

2. Invisibility. Vapor is invisible in dry weather and only faintly visible in damp weather.

3. Lack of odor. Practically odorless when pure and in ordinary field concentration.

4. Vapor pressure is low, but sufficient to establish lethal concentration at ordinary temperatures.

5. Boiling point is very high.

6. Vapor density is five times that of air.

7. Liquid density is below 1.5.

8. Melting point is not above maximum atmospheric temperatures. Hence use of solvent is advisable.

9. Very persistent, which increases its value in defense.

Chemical Properties.--

1. Chemical stability is high.

2. Hydrolyzes only very slowly at ordinary temperature and normal storage conditions.

3. Withstands explosion without decomposition.

Physiological Properties.--

1. High toxicity.

2. Extreme multiple effectiveness.

3. Effects of long duration but not permanent.

4. Effect is delayed from 6 to 24 hours, which reduces its offensive use.

5. Extremely insidious in action. No warning properties or symptoms.

6. Null rate of detoxification. Cumulative effect.

Other Properties.--

1. Extremely penetrative. It is absorbed by rubber and penetrates leather and ordinary textile fabrics. Into ordinary brickwork very little penetration, increased if material is very porous. Extremely penetrative to all forms of organic matter.

2. Not very difficult to manufacture. The process is now well known.

3. Ready availability of raw materials (chlorine, sulfur and ethylene).

4. It is capable of being disseminated from convenient devices.

5. It is difficult to gain protection from mustard gas and detection is not easy.

6. The mechanism of action, protective measures and method of treatment are well known.

From this study it may be seen how close mustard gas approaches the ideal battle gas in most of the important requirements.

From a more general viewpoint, considering mustard gas as a prospective agent, once this conclusion is made, the third step, that is experimental testing, would be effected with 90 per cent probability of success.

Mustard gas can be starting material for many syntheses, and due to this fact the properties and manufacturing methods of this substance are well known. This is one of the many examples of chemical agents with considerable economic value as raw material or intermediate products in several chemical processes. This is the main reason why Germany, with a fantastic development in its chemical industry, was in the First and Second World Wars far ahead in the discovery and production of new agents.

A strong chemical industry and an intelligent use of the tools that chemical engineering provides are the basis for a successful transformation of normal peacetime operations to the production of war gases.

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